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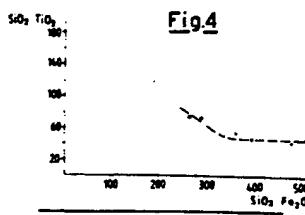
㉓ Synthetic, crystalline, porous material containing silicon oxide, titanium oxide and iron oxide.

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㉔ A crystalline, porous, synthetic material is disclosed, together with its related preparation process. Such a material of zeolitic character, containing silicon, titanium and iron oxides, corresponds, in its calcined and anhydrous state, to the following empirical formula

$p \text{HFeO}_2 \cdot q \text{TiO}_2 \cdot \text{SiO}_2$

wherein p has a value greater than zero and lower than or equal to 0.050, q has a value greater than zero and lower than or equal to 0.025, and the H^+ of HFeO_2 can be at least partly replaceable or replaced by cations.



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"SYNTHETIC, CRYSTALLINE, POROUS MATERIAL CONTAINING SILICON OXIDE, TITANIUM OXIDE AND IRON OXIDE"

The present invention relates to a synthetic material containing silicon oxide, titanium oxide and iron oxide, having a crystalline, porous, structure of zeolitic character and to the process for the preparation of such a material.

Such a material is structurally similar to ZSM-5 zeolite as disclosed in US-3,702,886 patent, formally constituted, in its calcined and anhydrous form, by $M_{2n}O_xSiO_4$, Al_2O_3 (with M = cation with n valency).

Other synthetic materials, structurally correlated to ZSM-5 zeolite are known, such as the one as disclosed in US-4,061,724 patent, formally constituted, in its calcined and anhydrous form, by SiO_2 , the one as disclosed in BE-886,812, formally constituted, in its calcined and anhydrous form, by SiO_2 and TiO_2 and the one as disclosed in FR-2,403,975 patent application, formally constituted, in its calcined and anhydrous form, by $M_{2n}O_xSiO_4$, Fe_2O_3 (with M = cation of n valency).

A novel synthetic zeolite has been found now, which we'll denominate "titanium-iron-silicalite", structurally similar to silicalite, which can be used either as molecular sieve or as ion exchanger, or as catalyst in the following reactions: cracking, selectoforming, hydrogenations and dehydrogenations, oligomerizations, alkylations, isomerizations, dehydrations of oxygen-containing organic compounds -selective hydroxylations of organic substrates by H_2O_2 (oxidation of olefins, hydroxylations of aromatics).

The synthetic, crystalline, porous material of zeolitic character, containing silicon, titanium and iron oxides, which is the object of the present invention, corresponds, in its calcined and anhydrous state, to the following empirical formula:



wherein p has a value higher than zero and lower than or equal to 0.050 and q has a value higher than zero and lower than or equal to 0.025,

and the H^+ of $HFeO_2$ can be at least partly replaceable or replaced by cations.

The passage from a cationic form to another cationic form can be performed by any customary exchange processes of the known art.

The synthetic material in accordance with the present invention results crystalline on X-ray examination.

Such an examination has been carried out by means of a powder diffractometer, equipped with an electronic impulse counter system, by using $CuK\alpha$ radiation. For the computation of the intensity values, the peak heights have been measured, and their percent heights relatively to the most intense peak have been computed.

The main reflections for the calcined and anhydrous product are characterized by the following d values (wherein d is the interplanar distance):

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	<u>d</u> <u>(\AA)</u>	Relative Intensity
40	11.14 + 0.10	vs
	9.99 + 0.10	s
45	9.74 + 0.10	m
	6.36 + 0.07	mw
	5.99 + 0.07	mw

50

	4.26 + 0.05	mw
	3.86 + 0.04	s
5	3.82 + 0.04	s
	3.75 + 0.04	s
	3.72 + 0.04	s
10	3.65 + 0.04	m
	3.05 + 0.02	mw
	2.99 + 0.02	mw

15 (wherein: vs = very strong; s = strong; m = medium; mw = medium-weak).

Such a diffraction spectrum is essentially similar to that of ZSM-5 and consequently of the other zeolites structurally correlated to ZSM-5, which have been mentioned in the introduction.

The material disclosed by ourselves shows an I.R. spectrum characterized by the following most representative values of wn (wherein "wn" is the wave number):

20

	wn ----cm ⁻¹ ----	Relative Intensity
25	1220 - 1230	w
	1080 - 1110	s
30	965 - 975	mw
	795 - 805	mw
	550 - 560	m
35	450 - 470	ms

(wherein: s = strong; ms = medium-strong; m = medium; mw = medium-weak; w = weak).

In Figure 1 the I.R. spectrum is shown, wherein on the abscissae the wave number in cm⁻¹ and on the ordinates the percent transmittance are expressed.

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Such an I.R. spectrum is essentially similar to that of the zeolite as disclosed in BE-886,812 patent, whilst it is considerably different from that of ZSM-5 (or from similar structures) and from that of the ferrosilicate as disclosed in FR-2,403,975 patent application, which have the I.R. spectrum as shown in Figure 2. It can be observed that in the spectrum of Fig. 2, the band at 965-975 cm⁻¹, which is characteristic of titanium silicalite of BE-886,812, and of titanium-iron-silicalite, does not appear.

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Summarizing, the material as disclosed by ourselves is different from ZSM-5 of US-3,702,886 and from the ferrosilicate as of FR-2,403,975 patent application, as to both its empirical formula and its I.R. spectrum; and relatively to the zeolite of BE-886,812 patent as to its empirical formula.

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Furthermore, the use of the subject material of the present invention as a catalyst in the above listed reactions is a further confirmation of the difference of our product relatively to those of the prior art.

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In fact, both ZSM-5 of US-3,702,886, and the ferrosilicate of FR-2,403,975 patent application can be used as catalysts in such reactions as dehydrations of oxygenated organic compounds, cracking, selectoforming, hydrogenations and dehydrogenations, oligomerizations, alkylations, isomerizations, but they result inactive in the reactions between organic substrates and H₂O₂, (hydroxylation of phenol to diphenols, oxidation of olefins), whilst the zeolite of BE-886,812 results inactive for the first reactions and active for the last ones; to the contrary, our zeolite is active for all of the above mentioned reactions.

A second object of the present invention is the preparation process for the obtainment of the synthetic, crystalline, porous material as defined above.

Said process is characterized in that under hydrothermal conditions a derivative of silicon, a derivative of titanium, a derivative of iron and a nitrogenous organic base are reacted, with an $\text{SiO}_2/\text{Fe}_2\text{O}_3$ molar ratio of the reactants greater than 50, preferably comprised within the range of from 150 to 600, an $\text{SiO}_2/\text{TiO}_2$ molar ratio of the reactants greater than 5, preferably comprised within the range of from 15 to 25, an $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio of the reactants preferably comprised within the range of from 10 to 100, more preferably of from 30 to 50, possibly in the presence of one or more salts and/or hydroxides of alkali or alkali-earth metals, with an M/SiO_2 molar ratio (wherein M is the alkali and/or alkali-earth cation) of the reactants lower than 0.1, preferably lower than 0.08, or equal to zero.

In the empirical formula of the material, the iron has been indicated in the HFeO_2 form, to underline that the material is in the H^+ form. When speaking of the ratios between the various reactants, we use, for iron, the Fe_2O_3 form, which is the most usual.

The silicon derivative is selected from silica gel, silica sol and alkyl silicates, among which, preferably, tetraethyl silicate; the titanium derivative is selected from titanium salts, such as, e.g., its halides, and organic titanium derivatives, such as, e.g., alkyltitanates, preferably tetraethyl titanate; the iron derivative is selected from iron salts, such as, e.g., its halides or the nitrates, the hydroxides, and the organic derivatives, such as, e.g., the alkoxides.

The nitrogenous organic base can be an alkylammonium hydroxide, preferably tetrapropyl-ammonium hydroxide.

In case tetrapropylammonium hydroxide is used, the $\text{TPA}^+/\text{SiO}_2$ ratio wherein $\text{TPA} =$ tetrapropylammonium of the reactants is comprised within the range of from 0.1 to 1, preferably from 0.2 to 0.4.

The reactants are reacted with each other by operating at a temperature of from 100° to 200°C, preferably of from 160° to 180°C, at a pH comprised within the range of from 9 to 14, preferably of from 10 to 12, and for a time period ranging from 1 hour to 5 days, preferably from 3 hours to 10 hours.

To the purpose of better illustrating the meaning of the present invention, some preparation and use examples are given, which in no way are to be considered as being limitative of the same invention.

Example 1

30 This example shows the preparation of titanium-iron-silicalite.

0.65 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is dissolved in water and from the solution the hydroxide is precipitated by means of the addition of ammonium hydroxide. The precipitate is filtered and washed by being redispersed in cold water, and filtered until the filtrate turns to neutral. The damp hydroxide is then dissolved in 54 g of solution at 18.7% by weight of tetrapropyl-ammonium hydroxide.

35 In a separate vessel, 2.28 g of tetraethyl-orthotitanate is dissolved in 41.6 g of tetraethyl-silicate and this solution is added to the previously prepared one, with stirring.

The whole mass is heated at 50-60°C, always with stirring, until a single-phase solution is obtained, then 100 cc of water is added.

40 The obtained solution is charged to an autoclave and is heated, under its autogenous pressure, at 170°C over 4 hours.

The discharged product is centrifuged and washed twice by re-dispersion and centrifuging; it is then dried 1 hour at 120°C, and is then calcined 4 hours at 550°C in the air.

The obtained product has an $\text{SiO}_2/\text{Fe}_2\text{O}_3$ molar ratio of 394, and an $\text{SiO}_2/\text{TiO}_2$ molar ratio of 48.

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Examples 2-6

In Table 1 other titanium-iron-silicalites are shown, which have been prepared by the same modalities as disclosed in Example 1, but with the composition of the reactants being varied.

50 From the above-reported preparation examples, one can observe that the maximum amounts of titanium and iron which can be obtained in the end product are not independent from each other.

The minimum $\text{SiO}_2/\text{TiO}_2$ ratio which can be obtained is of about 44, and it can be only obtained if $\text{O}_2/\text{Fe}_2\text{O}_3$ ratio in the reactant mixture is higher than about 250 (Examples 1, 2, 3).

55 By increasing $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio in the reactant mixture, a decrease of $\text{SiO}_2/\text{TiO}_2$ ratio and an increase of $\text{SiO}_2/\text{Fe}_2\text{O}_3$ occurs in the obtained product (Examples 5, 4, 1, 2, 3).

$\text{SiO}_2/\text{TiO}_2$ ratio in the obtained product continues to decrease until it reaches its minimum value around 44, which is reached when $\text{SiO}_2/\text{Fe}_2\text{O}_3$ in the reaction mixture is of from 250 to 600; further increases of $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio in the reactant mixture cause only $\text{SiO}_2/\text{Fe}_2\text{O}_3$ to increase in the obtained product, whilst $\text{SiO}_2/\text{TiO}_2$ remains nearly constant (Example 3).

5 The addition of alkali metals to the reaction mixture favours the decrease of $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio in the obtained product (Example 6) ratio in the obtained product.

Example 7

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Always in Table 1, a product is shown, which does not have the same characteristics as of the preceding products.

It can be observed from said Example that, when the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio in the reactant mixture is 30, in the absence of alkali metals no crystallization of the mixture occurs.

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Example 8

20 Always in Table 1, a product is shown, which has the I.R. spectrum of Fig. 3, from which it can be observed that the band at $965\text{-}975\text{ cm}^{-1}$ is only sparingly shown, with a much lower intensity than that in the spectrum of Fig. 1, although the product of Example 8 has a higher titanium content than of Examples 1-3.

The addition of large amounts of alkali metals ($\text{M}^+/\text{SiO}_2 = 0.08$) in the reaction mixture can cause an increase in titanium amount, which can be detected from the chemical analysis of the obtained product, an $\text{SiO}_2/\text{TiO}_2$ ratio lower than 40 being obtained, but in such case TiO_2 is at least partly in a form different from

25 the form it has in the titanium-iron-silicalite, and such as not to yield the spectrum of Fig. 1, but that of Fig. 3.

In Fig. 4, a chart is shown, which sets forth the dependence of the maximum amounts of titanium (shown in the ordinates as $\text{SiO}_2/\text{TiO}_2$, molar ratio) and of iron (shown in the abscissae as $\text{SiO}_2/\text{Fe}_2\text{O}_3$, molar ratio) which can be obtained in the end product.

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Table 1

Example	Reaction Mixture Composition				Crystallization time, hours	Crystallization Temperature, °C	Product Composition		
	SiO ₂ /Fe ₂ O ₃	SiO ₂ /TiO ₂	Na ⁺ /SiO ₂	TPA ⁺ /SiO ₂			SiO ₂ /Fe ₂ O ₃	SiO ₂ /TiO ₂	
1	250	20	-	0.25	40	4	170	394	48
2	600	20	-	0.25	40	4	170	474	43
3	1000	20	-	0.25	40	4	170	837	44
4	200	20	-	0.25	40	4	170	363	55
5	70	20	-	0.25	40	4	170	287	72
6	200	20	0.01	0.25	40	4	170	262	73
7	30	20	-	0.25	40	4	170	no crystallization	
8	70	20	0.08	0.25	40	15	170	54	23

Example 9

To a 1-l steel autoclave equipped with mechanical stirrer, temperature control system, pressure control system to operate under constant pressure, 70 g of water, 250 g of methanol, 4 g of catalyst prepared according to Example 2 are charged.

To a drum connected with the autoclave, 54 g of 34% (weight/weight) H_2O_2 is charged. After that the temperature of the system has been set at the controlled value of $40^\circ C$, and being pressurized with propylene at the pressure of 6 abs. atm. (constant throughout the test duration), the hydrogen peroxide is added, with strong stirring, to the suspension inside the autoclave.

The reaction is monitored by samples being drawn, at time intervals, and analysed. Hydrogen peroxide is determined to iodometric titration, and the reaction products are analysed by gas-chromatography.

After 1 hour the following situation has occurred:

H_2O_2 conversion : 95 %

Selectivity (relatively to H_2O_2),

propylene oxide : 80 %

1-methoxy-2-hydroxypropane : 11 %

2-methoxy-1-hydroxypropane : 5.5%

propylene glycol : 3.0%

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Example 10

The process is carried out by means of the equipment and the modalities of Example 9. The reactants used are 420 g of CH_3OH , 4 g of catalyst (prepared according to Example 2) and 41 g of 34% (weight/weight) H_2O_2 . The operating temperature is of $40^\circ C$ and the propylene pressure is of 4 abs. atm. After 45 minutes of reaction, the situation of the system is as follows:

H_2O_2 conversion : 93 %

Selectivity (relatively to H_2O_2),

propylene oxide : 83 %

30 1-methoxy-2-hydroxypropane : 10 %

2-methoxy-1-hydroxypropane : 5.5%

propylene glycol : 1 %

35 Example 11

To a 1-l steel autoclave, equipped with mechanical stirrer and reaction temperature control system, 450 g of methanol 90 g of 1-octene, 4.5 g of catalyst (prepared according to Example 2) are charged.

To a drum connected with the autoclave, 45 g of 34% (weight/weight) H_2O_2 is charged. After that the temperature of the system has been set at the controlled value of $45^\circ C$, and with stirring, hydrogen peroxide is added to the other reactants. The reaction course is monitored by samples being drawn at regular time intervals. Hydrogen peroxide is determined by iodometric titration, and the reaction products are analysed by gas-chromatography.

After 1 hour, the situation is:

45 H_2O_2 conversion : 90 %

Octene conversion : 50.3%

Selectivity to 1,2-epoxyoctane : 78 %

Ethers + glycols : 21.5%

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Example 12

The process is carried out by means of the same modalities and equipment as of Example 11.

To the autoclave, charged are 400 g of methanol, 90 g of allyl chloride, and 9 g of catalyst prepared according to Example 2; to the drum, 61 g of 34% (weight/ weight) H_2O_2 is added. The reaction is carried out at the temperature of $60^\circ C$. Thirty minutes later, the situation is:

H_2O_2 conversion : 95 %

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 Allyl chloride conversion : 49 %
 Epichlorohydrin selectivity (relatively
 to H_2O_2) : 80 %

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 Example 13

To a tubular steel reactor, 1.04 g is charged of catalyst of 18-40 mesh of granulometry, prepared according to Example 2. The reactor is placed inside an electrical oven and is gradually heated up to the reaction temperature, with a stream of dimethyl ether being flown through it. The gaseous reaction products are analyzed by in-line chromatography after the liquid products being condensed in a bath kept at 0-5°C. These latter are separately weighed and analyzed, always by chromatographic way. The conversion and selectivity are computed according to the hereunder shown equations:

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$$\text{Conversion} = \frac{(\text{DME}_{\text{in}} - \text{DME}_{\text{out}})}{(\text{DME}_{\text{in}})}$$

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$$\text{Selectivity} = \frac{(\text{mol of i product})}{(\text{DME}_{\text{in}} - \text{DME}_{\text{out}})}$$

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 (DME = dimethyl ether; in = incoming; out = outgoing).
 The reaction conditions and the results obtained are gathered in Table 2.

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Table 2

T	(°C)	360	380
P	(atm)	1	1

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	GHSV	(h ⁻¹)	440	800
5	Run hours		3	3
	DME Conversion (%)		86	84

Product Composition (% by weight - H₂O, DME excluded)

10	CH ₃ OH	11.0	67.2
	CH ₄	0.4	0.5
15	C ₂ H ₄	0.7	0.7
	C ₂ H ₆	0.01	0.01
	C ₃ H ₆	8.6	18.6
20	C ₃ H ₈	0.1	0.3
	ΣC ₄	2.7	9.6
	ΣC ₅	0.3	1.9
25	ΣC ₆ +	76.1	1.1

Claims

1. Synthetic, crystalline, porous material of zeolitic character, containing silicon oxide, titanium oxide and iron oxide, characterized in that
 30 it corresponds, in its calcined and anhydrous state, to the following empirical formula:
 $p \text{HFeO}_2 \cdot q \text{TiO}_2 \cdot \text{SiO}_2$
 wherein p has a value higher than zero and lower than or equal to 0.050 and q has a value higher than zero and lower than or equal to 0.025, the H⁺ of HFeO₂ can be at least partly replaceable or replaced by cations, in that it has the X-ray powder diffraction spectrum, the most meaningful lines of which are:
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	<u>d</u>	I_{rel}
	11.14 + 0.10	vs
5	9.99 + 0.10	s
	9.74 + 0.10	m
	6.36 + 0.07	mw
10	5.99 + 0.07	mw
	4.26 + 0.05	mw
	3.86 + 0.04	s
15	3.82 + 0.04	s
	3.75 + 0.04	s
	3.72 + 0.04	s
20	3.65 + 0.04	m
	3.05 + 0.02	mw
	2.99 + 0.02	mw

25 wherein d are the interplanar distances in Å and I_{rel} are their relative intensities, wherein vs means very strong; s means strong; m means medium; mw means medium-weak; w means weak, and that it shows an I.R. spectrum having at least the following bands:

	wn	I_{rel}
	1220 - 1230	w
35	1080 - 1110	s
	965 - 975	mw
	795 - 805	mw
40	550 - 560	m
	450 - 470	ms

45 wherein wn in the wave number in cm^{-1} and I_{rel} are the relative intensities, wherein s means strong; ms means medium-strong; m means medium; mw means medium-weak; w means weak.

50 2. Process for the preparation of the synthetic, crystalline, porous material according to claim 1, characterized in that under hydrothermal conditions a derivative of silicon, a derivative of titanium, a derivative of iron and a nitrogenous organic base are reacted, possibly in the presence of one or more salt(s) and/or hydroxide(s) of alkali or alkali-earth metal, with an $\text{SiO}_2/\text{Fe}_2\text{O}_3$ molar ratio of the reactants greater than 50,

55 an $\text{SiO}_2/\text{TiO}_2$ molar ratio of the reactants greater than 5, and an M/SiO_2 molar ratio (wherein M is the alkali or alkali-earth cation) of the reactants lower than 0.1, or equal to zero.

3. Process according to claim 2, wherein the $\text{H}_2\text{O}/\text{SiO}_2$ of the reactants is comprised within the ratio of from 10 to 100.

4. Process according to claims 2 and 3 wherein the $\text{SiO}_2/\text{Fe}_2\text{O}_3$ molar ratio of the reactants is comprised between 150 and 600, the $\text{SiO}_2/\text{TiO}_2$ molar ratio of the reactants is comprised between 15 and 25, the $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio of the reactants is comprised between 30 and 50 and the M/SiO_2 molar ratio of the reactants is zero.

5. Process according to claim 2, wherein the silicon derivative is selected from silica gel, silica sol and alkyl silicates, the titanium derivative is selected from the salts and the organic derivatives of titanium, the iron derivative is selected from the salts, the hydroxides and the organic derivatives of iron.

6. Process according to claim 5, wherein the alkyl silicate is tetraethyl silicate.

5 7. Process according to claim 5, wherein the titanium salts are halides.

8. Process according to claim 5, wherein the organic derivatives of titanium are alkyl titanates.

9. Process according to claim 8, wherein the alkyl titanate is tetraethyltitanate.

10. Process according to claim 5, wherein the iron salts are selected from halides and nitrates.

11. Process according to claim 5, wherein the organic derivatives of iron are the alkoxides.

10 12. Process according to claim 2, wherein the nitrogenous base is an alkylammonium hydroxide.

13. Process according to claim 12, wherein the alkylammonium hydroxide is tetrapropylammonium hydroxide.

14. Process according to claim 2, wherein the reactants are reacted by operating at a temperature comprised within the range of from 120° to 200°C, at a pH comprised within the range of from 9 to 14 and for a time period ranging from 1 hour to 5 days.

15. Process according to claim 14, wherein the reactants are reacted by operating at a temperature comprised within the range of from 160° to 180°C, at a pH comprised within the range of from 10 to 12 and for a time ranging from 3 hours to 10 hours.

16. Process according to claim 13, wherein the TPA^+/SiO_2 molar ratio of the reactants is comprised within the range of from 0.1 to 1.

17. Process according to claims 4, 5, 6, 9, 13, 15 and 16, wherein the TPA^+/SiO_2 molar ratio of the reactants is comprised within the range of from 0.2 to 0.4.

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Fig.1

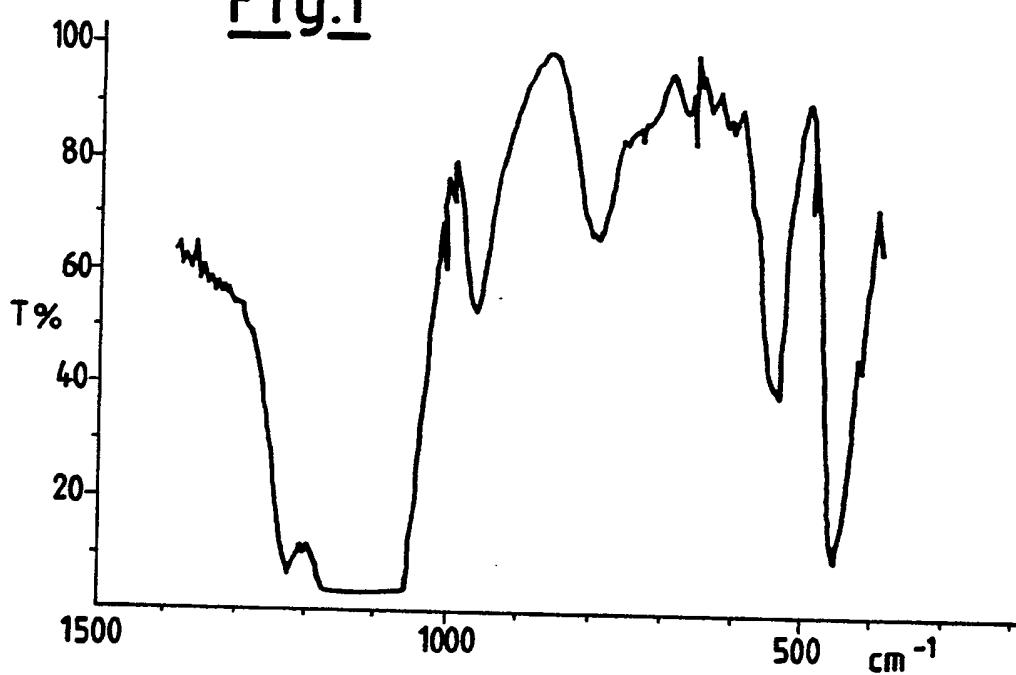


Fig.2

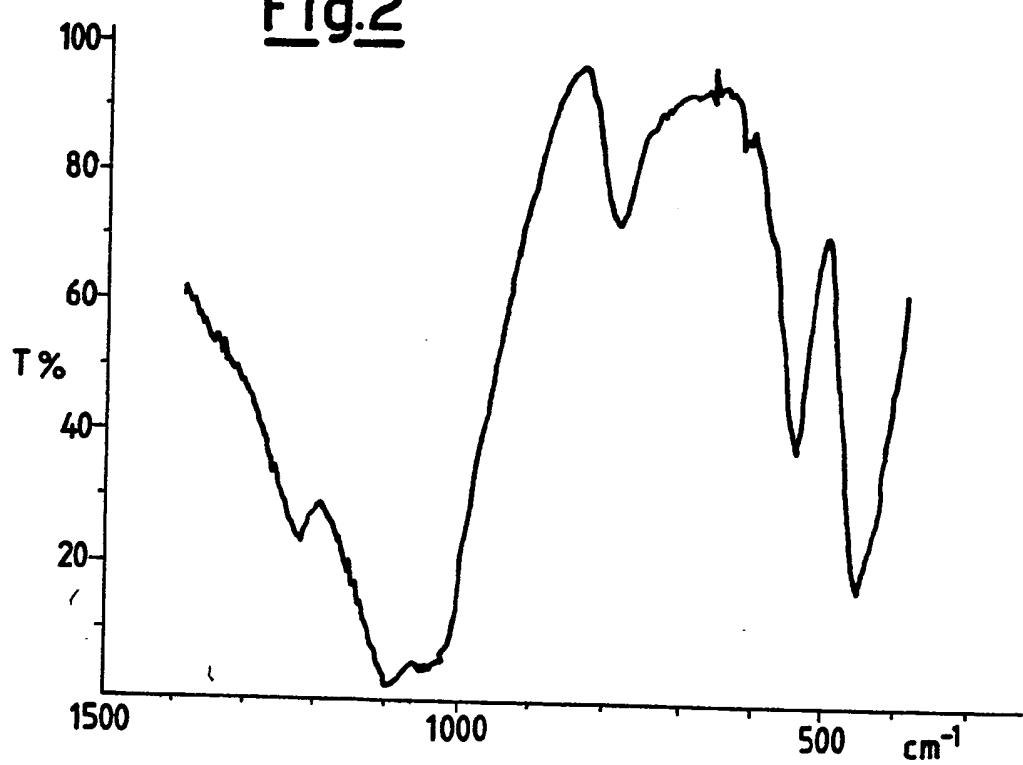


Fig.3

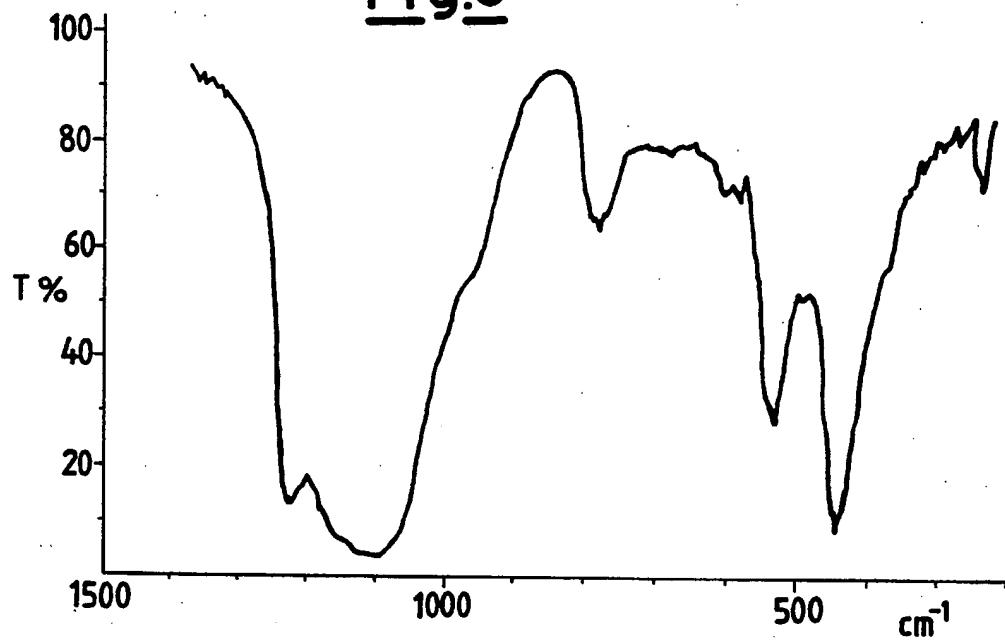
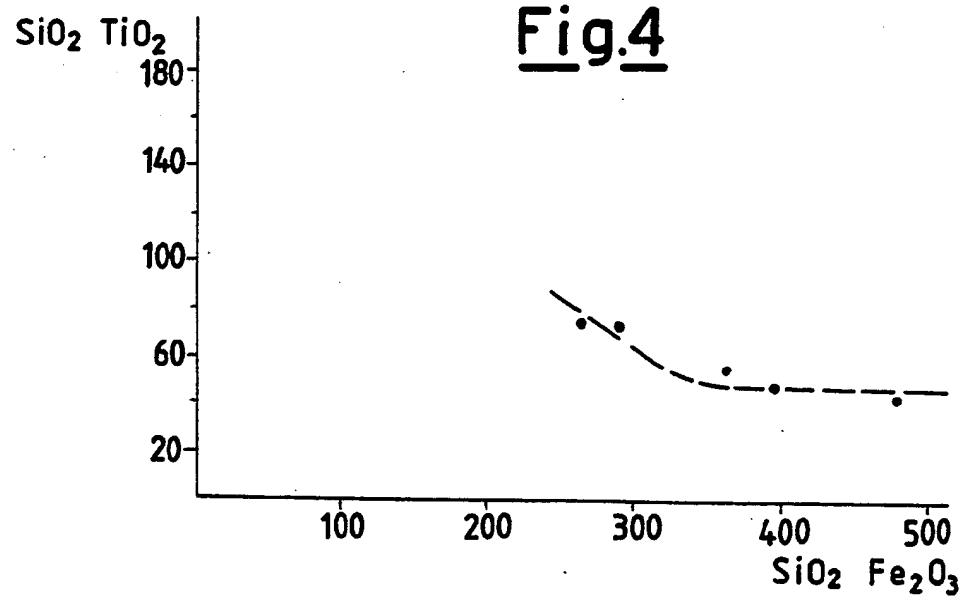
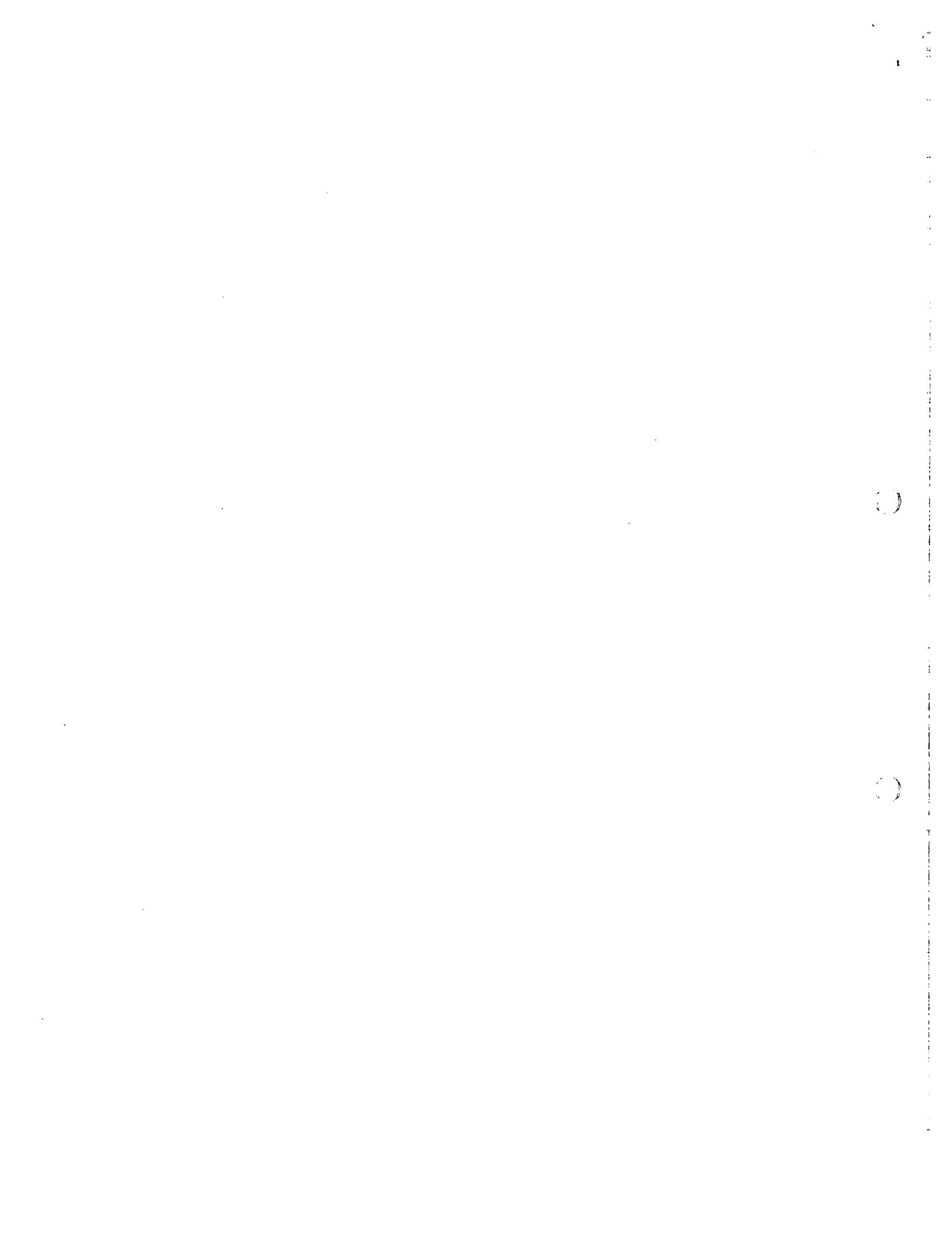


Fig.4







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EUROPEAN PATENT APPLICATION

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㉒ Synthetic, crystalline, porous material containing silicon oxide, titanium oxide and iron oxide.

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Such a material of zeolitic character, containing silicon, titanium and iron oxides, corresponds, in its calcined and anhydrous state, to the following empirical formula

$p \text{HFeO}_2 \cdot q \text{TiO}_2 \cdot \text{SiO}_2$

㉔ wherein p has a value greater than zero and lower than or equal to 0.050, q has a value greater than zero and lower than or equal to 0.025, and the H^+ of HFeO_2 can be at least partly replaceable or replaced by cations.

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DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)						
A	FR-A-2 471 950 (SNAMPROGETTI S.p.A.) & BE-A-886 812 (Cat. D,A) ---		C 01 B 33/20						
D,A	FR-A-2 403 975 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) ---								
A	CHEMICAL ABSTRACTS, vol. 103, no. 16, 21st October 1985, page 424, abstract no. 129920z, Columbus, Ohio, US; JP-A-60 65 714 (AGENCY OF INDUSTRIAL SCIENCES AND TECHNOLOGY) 15-4-1985 -----								
TECHNICAL FIELDS SEARCHED (Int. Cl.4)									
C 01 B 33/00									
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>22-02-1988</td> <td>BREBION J.CH.</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	22-02-1988	BREBION J.CH.
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THE HAGUE	22-02-1988	BREBION J.CH.							
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							

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